

Electronic Work Function of Melts of Na-K-Cs and Na-K-Rb Ternary Systems

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ABSTRACT

Wide use of alkali metals and their alloys in modern technology requires knowledge their physicochemical properties. In this paper we present the results of the experimental study of temperature and composition dependencies of electronic work function (EWF) of ternary alloys of the Na-K-Cs and Na-K-Rb systems, as well as Na-Cs and K-Cs binary alloys. Polytherms of EWF $\varphi(T)$ are linear with negative or positive temperature coefficients (TC) for the Na-K-Rb and Na-K-Cs systems over the temperature range from 300 to 420K. No extremums were found on the EWF isotherms at 298K, constructed as curves of equal values of EWF over the entire area of the composition triangle (isothermal surface).

INTRODUCTION

Study of the electronic work function (EWF) of alkali metals and their multicomponent alloys is of great importance in photoemission theory, in creating new power-intensive chemical current sources, highly effective photocathodes and charged particles sources, and so on [1,2]. An analysis of literature showed that the temperature and composition dependencies of EWF of such materials are studied insufficiently. For instance, the EWF of ternary alloys of alkali metals is not studied well enough [3,4].

TECHNIQUE FOR ELECTRONIC WORK FUNCTION MEASUREMENT

The work function was measured by the Fowler's photoelectric method, which yields an experimental error of about 1%. Automatic processing of the photocurrent data with a computer program ensured proper alignment of the experimental spectral dependencies with theoretical Fowler's curves.

The alloys were prepared using high purity metals with 99.995% content of the base element. Experiments were performed under 10^{-7} Pa vacuum condition in a completely sealed metered cell, constructed specifically for the study of EWF of alkali metals and their multicomponent melts [5]. Measurements were performed in steps of 1 to 3 degrees in the temperature range from 20 to 120°C. At each temperature the alloys were allowed to settle for at least half an hour in order for all possible structure transformations to complete.

RESULTS AND DISCUSSION

In this work, the experimental results on the electronic work function of 110 ternary alloys of the Na-K-Cs system and 40 ternary alloys of the Na-K-Rb system are presented. The ternary alloys were prepared by adding K to the initial Na-Cs binary alloy at constant

$X_{\text{Na}}:X_{\text{Cs}}$ ratio. The compositions of the studied alloys of the Na-K-Cs system are shown in Fig 1.

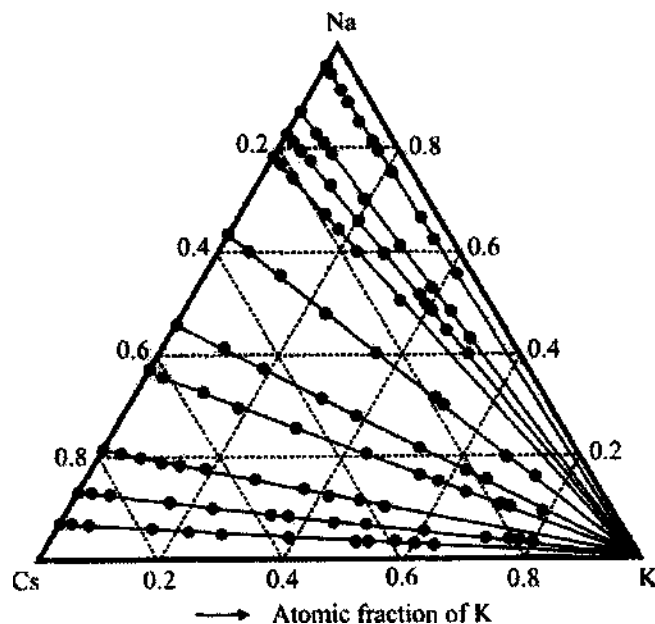


Fig 1. Compositions of the 110 ternary alloys of the Na-K-Cs system along the sections, for which the electronic work function was measured.

The studied alloys, formed along ten sections, cover the entire composition triangle. Polytherms of EWF of alloys over the studied temperature ranges are described by linear equations with positive or negative TC, depending on the composition of an alloy. For the alloys formed along the section with ratio $X_{\text{Na}}:X_{\text{Cs}} = 1:1$ and with 2.0 at.% content of K, the isotherms of EWF have a positive TC, equal to $3.4 \cdot 10^{-4}$ eV/K, while for other alloys along the same section the TC are negative.

Absolute values of TC for the alloys, prepared along the sections with $X_{\text{Na}}:X_{\text{Cs}} = 6:1$ and $X_{\text{Na}}:X_{\text{Cs}} = 1:1$, exhibit negative deviations from the additive curve. TC values increase when the content of Na in the ternary alloys increases. The positive TC of the polytherms for some Na-K-Cs and Na-K-Rb alloys may be explained by desorption of a surface-active component with increasing temperature.

In ternary alloys rich with Na the EWF decreased, when up to 20 at.% of K was added. However, if Na is replaced by Cs in the ternary alloys, K becomes a surface-inactive component. One can note, that addition of K to the Na-Rb alloys results in the increase of a photocurrent by an order of magnitude. The isotherms of the EWF of Na-K-Cs alloys with constant $X_{\text{Na}}:X_{\text{Cs}}$ ratio at 313K are shown in Fig.2. The isotherms do not exhibit any extremums. The polytherms of EWF of the studied binary alloys were also obtained. For all

Na-Rb alloys and Cs-rich Na-Cs and K-Cs alloys they are satisfactorily described by linear equations with negative TC. Temperature coefficients are positive for alloys containing small amounts of Cs due to desorption of Cs from the surface layer with increasing temperature. The concentration dependencies of the temperature coefficients of the EWF for alloys are complicated: their absolute values reveal a large scatter and oscillations. With increasing temperature, the changes in EWF appear to depend on two factors. Firstly, structural changes weaken interatomic bonds and reduce the electrical barrier on the surface layer. Secondly, the surface layer composition changes due to desorption of the surface-active component.

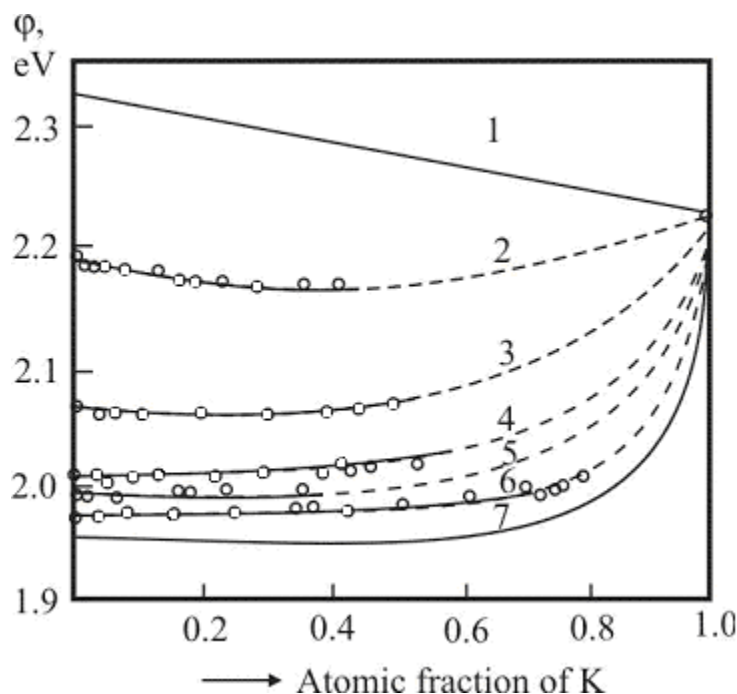


Fig.2. Isotherms of electronic work function at 313K for alloys: 1 - Na-K; 2 – $X_{Na}:X_{Cs}=58:1$; 3 - 14:1; 4-6:1; 5-4:1; 6-1:11; 7-Cs-K.

The first factor leads to a reduction of the EWF, while the second results in an increase of the EWF of the alloys. Cs is a surface-active component in the Na-Cs and K-Cs systems. Therefore, if the bulk concentration of Cs is small, its concentration in surface layer decreases sharply with increasing temperature, leading to an increase of the EWF. If the bulk concentration of Cs reaches 15-20 at.%, the desorption of Cs has only a slight influence on the composition of the surface layer, resulting in an increasing role of the structure factor.

More detailed study of the EWF of the Na-Cs system with 0 to 50 at.% content of Cs revealed a complicated character of the EWF isotherm at -90°C in the range of Cs concentration from 0 to 15 at.%. Our results do not exhibit a minimum near 32.4 at.% Cs. The K-Cs system has a phase diagram with an azeotropic minimum, so one would expect

appreciable changes in the EWF in the range of small concentrations of the components (Fig 3).

Addition of up to 25-30 at. % of Cs results in a decrease of the EWF to a value close to that of a pure Cs (~ 1.95 eV). Further addition of Cs does not change EWF values of the alloys. More detailed study of the EWF in the concentration ranges 0 - 20 at.% and 70 - 100 at.% of Cs showed that addition of up to 2 at.% of Cs to K leads to EWF values sharply decreasing toward that of a pure Cs. Our results are in satisfactory agreement with theoretical calculations performed using the electron density functional method [6].

The curves of the equal EWF values (isolines) for the Na-K-Cs alloys at 298K are presented in Fig.3.

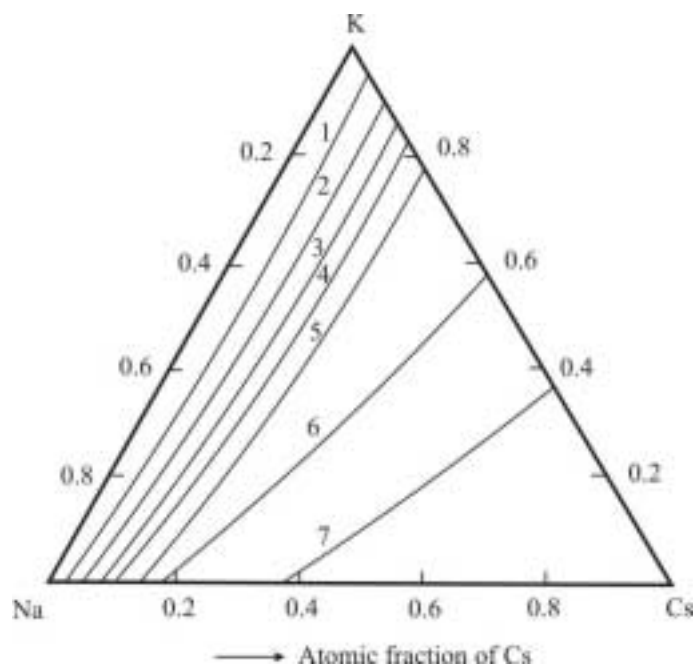


Fig.3 Curves of equal values of the EWF of the Na-Cs-K alloys at 298 K: 1 - 2,15; 2 - 2,04; 3 - 2,02; 4 - 2,00; 5 - 1,98; 6 - 1,97; 7 - 1,96 eV. Values of the EWF for Na, K and Cs at 298K are 2.41, 2.28 and 1.95 eV, respectively.

CONCLUSION

Polytherms of the EWF for the Na-Cs-K and Na-Rb-K systems over the studied temperature range are described by linear equations with positive and negative temperature coefficients. The temperature and concentration dependencies of the EWF of the Na-Cs and K-Cs alloys were measured. No extremums were found on the EWF isotherms of the Na-Cs system at -90°C , and the Na-Cs-K and Na-Rb-K systems at 298K.

Our results showed both absence of any extremum in the concentration dependence of the EWF for systems with eutectic alloys and the effect of chemical composition on the shape of a EWF isotherm at low temperatures only.

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